

# **Photochemical Sinks Of Organic Pollutants In Estuarine And Near-Shore Environments**

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## **LONG-TERM GOALS**

A principal objective of this work is to assess the quantitative importance of homogeneous and heterogeneous photochemistry as a sink of pollutants in the aquatic environment. In particular, we ultimately hope to develop a predictive model for the photochemical degradation of hydrophobic organic pollutants (HOPs) in natural waters, based on correlations between the redox properties of selected series of HOPs and the rates and wavelength dependence of their heterogeneous photodegradation by colored dissolved organic matter (CDOM).

## **OBJECTIVES**

Our specific objectives for this project are as follows:

- Establish a much better mechanistic understanding of the primary photophysical and photochemical events occurring within the CDOM and how these events are affected by HOP binding. A combination of steady-state and time-resolved spectroscopic techniques and radical trapping methods will be employed to examine the wavelength dependence of these processes.
- Employ a series of both polar and hydrophobic chlorinated compounds with differing one-electron reduction potentials to probe the ability of CDOM to photoreduce these compounds (reductive dechlorination). Employ two series of PAHs - one with approximately constant singlet energy but varying thermodynamic driving force for electron transfer and one with approximately constant driving force but varying singlet energy - to test the mechanism of the fluorescence quenching of PAHs bound to CDOM. We plan to use these two series of compounds to establish whether a quantitative relationship exists between the rates of PAH photodegradation and their redox potentials, and to probe the oxidizing and reducing power of photoexcited CDOM.

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- Measure the wavelength dependence of the quantum yields for the photodegradation of selected HOPs within these series in the presence of CDOM standards and in natural waters. The rates of HOP photodegradation under broad-band irradiation (sunlight or simulated sunlight) will also be acquired and compared with those calculated from the spectral dependence of the quantum yields. Gas chromatography (GC) and GC/mass spectrometry (GC/MS) will be employed to follow the loss of the HOPs and the formation of products.
- Use the combined data sets to develop a predictive model for the heterogeneous photodecomposition of HOPs by CDOM. Ultimately, we hope to be able to predict roughly the spectral dependence for the rates of HOP photodegradation in the environment, given the one-electron oxidation or reduction potential of the pollutant and assuming that CDOM from different environments exhibits similar photochemical properties. This model can be tested by examining the photodegradation of HOPs not included in the development of the model.

## APPROACH

Steady-state and time-resolved spectroscopic techniques, chemical trapping methods, and an array of photochemical analyses are or will be employed to determine the quantitative importance of homogeneous and heterogeneous photochemistry as a sink of organic pollutants in the near-shore environment. Laser flash photolysis (LFP) and time-resolved fluorescence techniques are being used to examine the primary photochemical events in CDOM and will ultimately be employed to study HOP-CDOM complexes. Currently, LFP is being used to determine the yield and the decay kinetics of  $e_{(aq)}^-$  from CDOM as a function of wavelength under anaerobic conditions (see Fig. 1). These yields will be compared with those obtained by a new chemical trapping method for determining  $e_{(aq)}^-$  (Thomas-Smith and Blough, in preparation). This method employs the rapid reaction of  $N_2O$  with the hydrated electron to form OH, followed by the reaction of OH with dimethylsulfoxide to generate a methyl radical, which is then trapped by an amino-nitroxide; following derivatization with fluorescamine this product is separated by reversed-phase high performance liquid chromatography and quantified fluorometrically (see for example, Kieber and Blough, 1990; Li et al., 1997; Vaughan and Blough, 1998). Another, potentially much simpler approach, employs the rapid reaction of  $e_{(aq)}^-$  with monochloromethane to produce the methyl radical directly, which is then trapped by the nitroxide and analysed as above (Fasnacht and Blough, work in progress).

Previous steady-state trapping studies of  $e_{(aq)}^-$  have shown that the rates of its formation at 355 nm are far smaller than those for  $O_2^-$  and  $H_2O_2$ . This result indicates the presence of a significant additional pool of reducing intermediate(s). Other than the ability of this pool to reduce  $O_2$  to  $O_2^-$ , nothing is known about its capability of reducing pollutants. To map the photoreducing potential of the CDOM, a series of mono-, di-, tri- and tetrachlorinated compounds (monochloromethane, dichloromethane, chloroform and carbon tetrachloride) are being examined. Because increasing halogen substitution makes these compounds easier to reduce, the yield of carbon-centered radicals produced by one-electron reduction (and determined by nitroxide trapping) is anticipated to increase with increasing halogen substitution, if the photochemical equivalents generated within the CDOM are sufficiently reducing.

We are also examining the photochemical production of strong oxidants by CDOM and its role in pollutant degradation. Our approach for detecting and quantitating OH production employs the rapid

reaction of OH with dimethylsulfoxide to produce quantitatively a methyl radical, which then reacts with an amino-nitroxide to produce a stable, O-methylhydroxylamine. Following derivatization with fluorescamine, this radical adduct is separated by reversed-phase HPLC and quantified fluorometrically. Unlike many previous OH detection methods, this method can be employed under both aerobic and anaerobic conditions and thus, can be used to test whether the presence of dioxygen is required for OH formation.

## WORK COMPLETED

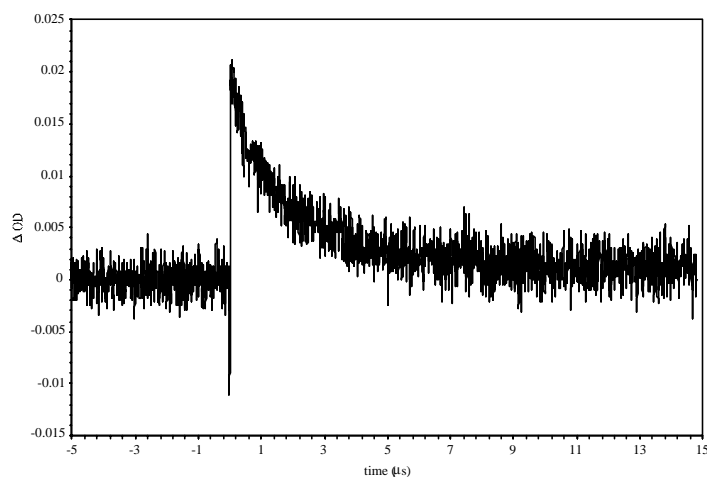
1). With support from the ONR (funded by this effort) and the NSF, a new Nd:Yag laser and dye laser head was acquired and incorporated in the flash photolysis system. This system will allow us to examine the wavelength dependence of transient intermediate formation by excitation of CDOM, HOPs or CDOM/HOP complexes throughout much of the ultraviolet wavelength regime. Work is proceeding on this task.

2) The method developed for determining  $e_{(aq)}^-$  using  $N_2O$  as the primary reactant was applied to acquire the wavelength-dependence of the quantum yields for  $e_{(aq)}^-$  production, both in solutions of fulvic acids and in natural waters. We have shown that the intermediate radicals generated by reaction of  $e_{(aq)}^-$  with monochloromethane and chloroform can be trapped by nitroxides and separated using HPLC; structural confirmation of the products is in progress.

3) The possible role of quinoid moieties within the CDOM acting as a photochemical source of OH or an oxidant exhibiting similar reactivity was examined using a method previously developed for OH detection (Vaughan and Blough, 1998).

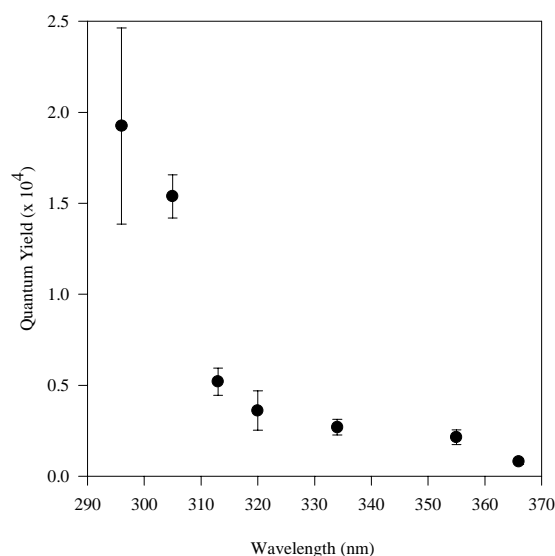
## RESULTS

1) LFP has been used preliminarily to determine the yield and decay kinetics of  $e_{(aq)}^-$  for both a model system (ferrocyanide photoionization) and for Suwanee River Fulvic Acid (355 nm excitation; Fig. 1). Work is proceeding on determining the wavelength dependence not only of  $e_{(aq)}^-$  production, but also of the formation of other transient intermediates.



**Figure 1. Waveform showing the production and decay of  $e_{(aq)}^-$  detected at 700 nm.  $e_{(aq)}^-$  produced by 10 mg/L SRFA after signal averaging with 20 shots from excitation at 355 nm.**

2) The carbon-centered radicals produced by reaction of the hydrated electron (formed by photolysis of ferrocyanide) with monochloromethane and chloroform have been trapped, separated and identified by HPLC. The reaction of  $\text{N}_2\text{O}$  with the hydrated electron to form OH, followed by the reaction of OH with dimethylsulfoxide to form a methyl radical which is subsequently trapped with an amino-nitroxide, has been used to obtain the wavelength dependence of the quantum yields for  $e_{(\text{aq})}^-$  production by SRFA and CDOM in a number of natural waters (Fig.2). Quantum yields for  $e_{(\text{aq})}^-$  production by SRFA and natural waters decrease substantially with increasing wavelength, varying from  $\sim 2 \times 10^{-4}$  at 296 nm to  $\sim 2 \times 10^{-5}$  at 355 nm. The yields at all wavelengths are significantly smaller than the yields for  $\text{O}_2^-$  and  $\text{H}_2\text{O}_2$  production, arguing that there is indeed a substantial pool of reducing equivalents not related to  $e_{(\text{aq})}^-$ . Thus, the ability of CDOM to reductively de-chlorinate a series of chlorinated compounds with differing one-electron reduction potentials is currently being examined to characterize this pool.



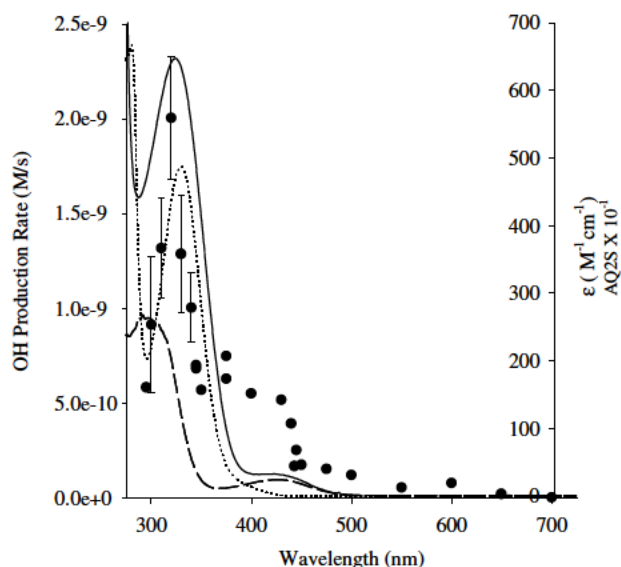
**Figure 2. Wavelength dependence of quantum yield for anaerobic hydrated electron production from SRFA. Error bars represent one standard deviation from mean value ( $n \geq 5$ ). Samples consist of SRFA (12 mg/L), 10 mM DMSO, 50  $\mu\text{M}$  3-ap and are saturated with  $\text{N}_2\text{O}$ .**

3) Using a previously developed technique (Vaughan and Blough, 1998), the action spectrum acquired for photochemical OH production from SRFA was found to be consistent with a role for quinoid moieties in this production (Fig. 3). However, model studies examining the photochemistry of the 1,4-benzoquinones and the 9,10-anthroquinones indicate that the oxidant produced does not exhibit the same reactivity profile as OH and may instead be an intermediate photosolvate (Vaughan and Blough, in preparation). Further work to resolve this issue is planned.

## IMPACT/APPLICATIONS

Knowledge of the rates and mechanisms of removal of pollutants from the environment is critical for establishing their long-term impact on aquatic ecosystems. Unfortunately, because of the diverse suite of compounds released, it is usually infeasible to assess the quantitative importance of all sinks for every compound. Moreover, new compounds are being created on a daily basis. A solution to this problem resides in the ability to predict the behavior of broad classes of compounds based on unifying

chemical principles. Such an approach is being applied in this study. The development of robust relationships between the environmental rates of the CDOM-sensitized photodegradation of HOPs and the more readily-acquired molecular properties of the HOPs such as redox potentials and/or singlet energies may allow us to produce models capable of predicting the photochemical fate of HOPs in natural waters. These simple models could then be integrated into ecosystem-wide HOP fate models to improve our ability to predict HOP distribution and loss.



**Figure 3. Comparison of the action spectra (●) for  $\bullet$ OH production rates to absorption spectra for several quinones (methyl-1,4-benzoquinone (-); 1,4-benzoquinone (---); anthraquinone-2-sulfonate(···)).**

The radical trapping approach described in this work, although originally developed with ONR support for application to the sensitive detection and identification of radicals in environmental systems (Blough and Simpson, 1988), has now been applied successfully to important problems in the biological sciences (eg., Pou et al., 1993; Kalai et al., 1998; Hideg et al., 1998; Li et al., 1999a, 1999b) and in polymer chemistry (eg., Gerlock et al., 1993; Moad et al., 1999).

## RELATED PROJECTS

In a related, ONR-supported project, we are examining the factors controlling the distribution and dynamics of CDOM in estuarine and coastal waters through a combination of field and laboratory measurements. As CDOM is the principal photoreactive constituent of most natural waters, an understanding of the factors which control its distribution in the environment is essential for determining the impact of photochemical processes in the remineralization of both natural and anthropogenic compounds.

## REFERENCES

- Blough, N.V. and D.J. Simpson (1988). Chemically mediated fluorescence yield switching in nitroxide-fluorophore adducts: optical sensors of radical/redox reactions. *J. Am. Chem. Soc.*, **110**, 1915–1917.
- Gerlock, J.L., P.J. Zemanidis, D.R. Bauer, D.J. Simpson, N.V. Blough, and I.T. Salmeen (1990). Fluorescence detection of free radicals by nitroxide scavenging. *Free Rad. Res. Comm.*, **10**, 119–121.
- Hideg, E., T. Kalai, K. Hideg and I. Vass (1998). Photoinhibition of photosynthesis in vivo results in singlet oxygen production; detection via nitroxide-induced fluorescence quenching in broad bean leaves. *Biochemistry*, **37**, 11405–11411.
- Kalai, T., E. Hideg, I. Vass and K. Hideg (1998). Double (fluorescent and spin) sensors for detection of reactive oxygen species in the thylakoid membrane. *Free Rad. Biol. Med.*, **24**, 649–652.
- Kieber, D.J. and N.V. Blough (1990). Determination of carbon-centered radicals in aqueous solution by liquid chromatography with fluorescence detection. *Anal. Chem.*, **62**, 2275–2283.
- Li, B., P.L. Gutierrez and N.V. Blough (1997). Trace determination of hydroxyl radical in biological systems. *Anal. Chem.*, **69**, 4295–4302.
- Li, B., P.L. Gutierrez and N.V. Blough (1999). Trace determination of hydroxyl radical using fluorescence detection. *Methods Enzymol.*, **300**, 202–216.
- Li, B., P.L. Gutierrez, P. Amstad and N.V. Blough (1999). Hydroxyl radical production by mouse epidermal cell lines in the presence of quinone anti-cancer compounds. *Chem. Res. Toxicol.*, in press.
- Pou, S., Y. Huang, A. Bhan, V.S. Bhadti, R.S. Hosmane, S.Y. Wu, G. Cao and G.M. Rosen (1993). A fluorophore-containing nitroxide as a probe to detect superoxide and hydroxyl radical generated by stimulated neutrophils. *Anal. Biochem.*, **212**, 85.
- Moad, G., D.A. Shipp, T.A. Smith and D.H. Solomon (1999). Measurements of primary radical concentrations generated by pulsed laser photolysis using fluorescence detection. *J. Phys. Chem. A*, **103**, 6580–6586.
- Vaughan, P.P. and N.V. Blough (1998). Photochemical formation of hydroxyl radical by constituents of natural waters. *Environ. Sci. Technol.*, **32**, 2947–2953.